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# Exhaust Gas Scrubber Washwater Effluent

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## EXECUTIVE SUMMARY

This document contains information about effluent washwater discharges associated with the operation of exhaust gas cleaning systems (EGCSs), also known as sulfur oxide (SO<sub>x</sub>) scrubbers, onboard vessels. The use of scrubbers to clean the exhaust from marine engines using high sulfur residual oil and diesel fuels is an option for reducing SO<sub>x</sub> air emissions required by Annex VI of the MARPOL International Convention for the Prevention of Pollution from Ships. Washwater generated by an EGCS can contain contaminants from three sources:

1. Pollutants scavenged from the exhaust gas exiting the engine (combustion products, fuel and lubricants);
2. The source of washwater used to clean the exhaust (seawater or freshwater); and
3. The scrubber itself (dissolution of materials, possible reaction products and/or chemical additives).

The deployment of SO<sub>x</sub> scrubbers to treat emissions from diesel engines on large ocean going vessels has been so far limited to a handful of ships. However, the use of SO<sub>x</sub> scrubbers in combination with high sulfur residual oil fuels may be an economically attractive option in Sulfur Oxide Emission Control Areas (SECAs) and worldwide. As the deadlines for SO<sub>x</sub> reduction<sup>1</sup> draw nearer, some vessels may begin using scrubbers to reduce SO<sub>x</sub> emissions rather than burning low sulfur fuel oil.

This document describes the basic technology of EGCS, treatment processes used to remove pollutants from washwater prior to discharge, guidelines established by the International Maritime Organization (IMO) for washwater monitoring and discharge criteria, available onboard sampling data characterizing the constituent concentrations in washwater discharge, and impacts of scrubber washwater discharge on water quality and aquatic life and protectiveness of IMO guidelines.

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<sup>1</sup> The revised Annex VI entered into force on July 1, 2010. The sulfur content of fuel will fall in the Emission Control Areas (ECAs), which include the Baltic Sea, the North Sea and the English Channel, from 1.5% to 1% in July 2010 and to 0.1% in January 2015. A North American ECA, which includes waters adjacent to the Pacific, Atlantic and Gulf coasts and the 8 main Hawaiian Islands, will become enforceable in 2012. Globally, the highest permitted sulfur content of fuel will fall from 4.5% to 3.5% in January 2012 and to 0.5% in January 2020.

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## SECTION 1

### INTRODUCTION

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The International Convention for the Prevention of Pollution from Ships (MARPOL), 1973 as modified by the Protocol of 1978, also known as MARPOL 73/78, Annex VI Prevention of Air Pollution from Ships, requires the reduction of SO<sub>x</sub> emissions either by burning low sulfur fuel oil or cleaning the exhaust gas. Cleaning, or scrubbing, the exhaust gas is generally accepted to be more economical. According to EGCS manufacturer Wärtsilä, the cost saved by using heavy fuel oil instead of low sulfur fuel oil can pay back the cost of installing and operating EGCS in about one year (Hatley, 2010). The EGCSs used today for sulfur control are commonly known as SO<sub>x</sub> scrubbers. In a wet scrubber, the exhaust gas is mixed with washwater, and the water-soluble components of the exhaust gas are removed by dissolution into the washwater. SO<sub>x</sub> scrubbers are capable of removing up to 95 percent of SO<sub>x</sub> from ship exhaust (EGCSA, 2010). By removing sulfur from the exhaust, the scrubber also removes most of the direct sulfate particulate matter (PM). Sulfates are a large portion of the PM from ships operating on high sulfur fuels. By reducing the SO<sub>x</sub> emissions, the scrubber also controls much of the secondary PM that is formed in the atmosphere from these emissions.

There are two main types of wet scrubber technologies. The first wet scrubber technology, referred to as seawater scrubbing, is an open-loop design which uses seawater to scrub the exhaust before discharging the washwater back to the sea following treatment. In a seawater scrubber, the exhaust gases are brought into contact with seawater, either through spraying seawater into the exhaust stream or routing the exhaust gases through a water bath. The sulfur dioxide (SO<sub>2</sub>) in the exhaust gas dissolves in the washwater, where it is ionized to bisulphate and sulfite, which are then readily oxidized to sulfate (Hassellöv and Turner, 2007). The ionization of SO<sub>2</sub> and the sulfuric acid formed from sulfur trioxide (SO<sub>3</sub>) also produces acidity. The sulfuric acid in the water then reacts with carbonates and other salts in the seawater to form sulfates (USEPA, 2009a). The washwater is treated to remove solids and raise the pH prior to discharge back to sea. The removed solids are stored onboard for shoreside disposal.

The second wet scrubber technology is a closed-loop system. Freshwater is used as washwater, and caustic soda is injected into the washwater to neutralize the sulfur in the exhaust. A small portion of the washwater is bled off and treated to remove suspended solids. The suspended solids are held as sludge and disposed of shoreside as with the open loop design. The treated bleed-off washwater can be discharged at open sea or held onboard for disposal shoreside. Additional freshwater is added to the system as needed. While this design is not a completely closed loop, it can be operated in zero discharge mode for a period of time (USEPA, 2009a).

Wet scrubbers are a well-established technology for SO<sub>x</sub> and PM reduction that are widely used in stationary sources such as land-based oil- and coal-fired power plants. In these applications, lime and caustic soda are typically used to neutralize the sulfuric acid in the washwater. The first use of exhaust gas scrubbers in the marine industry was not for SO<sub>x</sub> emission control but rather as an inexpensive means to produce inert gas for reducing the fire hazard in the cargo tanks of tankers while unloading. By the 1970s, their use was widespread (Entec, 2005).

The first prototype seawater scrubber system for exhaust gas control onboard a vessel was installed in 1991 (Entec, 2005). A comprehensive seawater scrubber field trial was conducted in May 1998 onboard the Canadian ice breaker *Louis S. St.-Laurent*. The trials were conducted during 22 days of a 6-week transatlantic voyage. Around the same time, a different scrubber prototype, the Eco-Silencer<sup>®</sup>, was fitted for testing onboard the Canadian freight and passenger ferry *Leif Ericson*. This was a full-scale plant and treated the entire exhaust stream from the engine. One of the specific aims of the *Leif Ericson* trials was to investigate washwater quality through a water treatment plant and, if necessary, apply alternate water treatment processes (Entec, 2005). More recent prototype SO<sub>x</sub> scrubber installations aboard three ships, the *Zaandam*, the *Pride of Kent* and the *Suula*, have demonstrated their viability in this application and provided data to characterize pollutant concentrations in scrubber washwater discharges. These demonstrations have shown that scrubbers can replace and fit into the space occupied by the exhaust silencer units and can work well in marine applications (USEPA, 2009a).

The deployment of SO<sub>x</sub> scrubbers to treat emissions from the diesel engines on large ocean going vessels is currently limited to a handful of ships. Although the installation of an EGCS allows a ship operator to continue to use high sulfur fuel after the 2015 and 2020 deadlines for ECAs and worldwide, respectively, there is uncertainty associated with this compliance solution (Kehoe et al., 2010). The continued use of EGCS depends on the successful completion of monitoring specified in the IMO Guidelines (see Section 4) and long-term scientific studies to prove they do not negatively impact the environment. In the interim, a ship owner installing EGCS undertakes a risk that the EGCS may need to be removed in favor of using low-sulfur fuel if in the future it is found that scrubbers have unacceptable impacts.

The use of SO<sub>x</sub> scrubbers in combination with high sulfur residual oil and diesel fuels may be economically beneficial in SECAs and worldwide; therefore, a large number of vessels may begin using scrubbers. In June 2010, the Motorship Newsletter announced the first commercial order for seawater scrubbers capable of meeting new European Union (EU) regulations on fuel emissions from ships, without requiring low sulfur fuel oil (Motorship Newsletter, 2010). Seawater scrubbers were installed on four new 45,000-ton ferries burning residual fuel oil to meet rules demanding sulfur emissions equivalent to 0.1 percent fuel-sulfur content.

This document describes the constituent concentrations in the washwater discharged by vessels operating wet scrubber EGCSs. This discharge can contain material from:

- Pollutants scavenged from the exhaust gas exiting the engine (combustion products, fuel and lubricants);
- The seawater used to clean the exhaust (in the case of a seawater scrubber); and
- The scrubber itself (dissolution of system materials, possible reaction products and/or chemical additives).

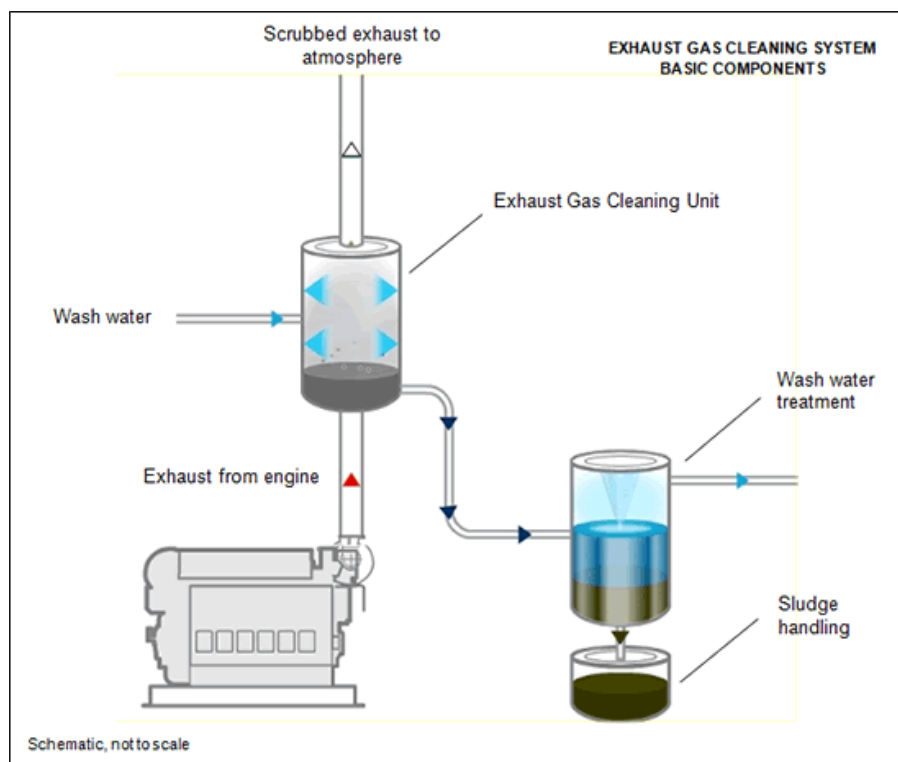
The use of scrubbers to clean the exhaust from marine engines using high sulfur residual oil and diesel fuels may lead to high concentrations of a number of harmful compounds in the water body around the ships (AEA, 2009). Several trials were conducted onboard vessels to characterize the constituent concentrations in washwater discharge. Section 5 summarizes the results of the trials and assessments of the potential impacts of scrubber washwater discharge on water quality and aquatic life. Section 6 presents a comparison of the results of the trials with the 2009 *Guidelines for Exhaust Gas Cleaning Systems* (IMO Annex 9, Resolution MEPC.184(59), adopted July 17, 2009), criteria intended to protect aquatic resources from adverse impacts resulting from scrubber washwater discharges.



## SECTION 2

### EXHAUST GAS SCRUBBER TECHNOLOGY

As described in Section 1, there are several different designs of SO<sub>x</sub> scrubbers that remove sulfur oxides from the exhaust gases of vessel engines and boilers. The majority of wet scrubber systems have three basic components, illustrated in Figure 1 and described below.



Source: EGCSA. 2010

**Figure 1. SO<sub>x</sub> Scrubber Components**

1. Exhaust gas cleaning unit serves as a contact chamber that enables the exhaust stream from an engine or boiler to be intimately mixed with water, either seawater, freshwater, or both. Due to space and access limitations, the exhaust gas cleaning units tend to be high in the ship, in or around the funnel area.
2. Wash water treatment to remove water-soluble pollutants, such as sulfur dioxide (SO<sub>2</sub>), sulfur trioxide (SO<sub>3</sub>) and nitrogen dioxide (NO<sub>2</sub>), which form sulfates and nitrates that dissolve in the washwater after the scrubbing process. Scrubber washwater also contains suspended solids, heavy metals, hydrocarbons and polycyclic aromatic hydrocarbons (PAHs). Before the washwater is discharged, it must be treated to remove solids. The treatment process typically includes a multicyclone, a cyclonic separator similar to that used to separate water from

residual fuel prior to delivery to the engine. Heavier particles may also be trapped in a settling or sludge tank for disposal.

3. Sludge handling to retain sludge removed by the washwater treatment process for disposal shoreside.

Figure 2 shows the EcoSilencer<sup>®</sup> scrubber incorporated into the exhaust train on the ferry *Pride of Kent*.



Source: Entec, 2005

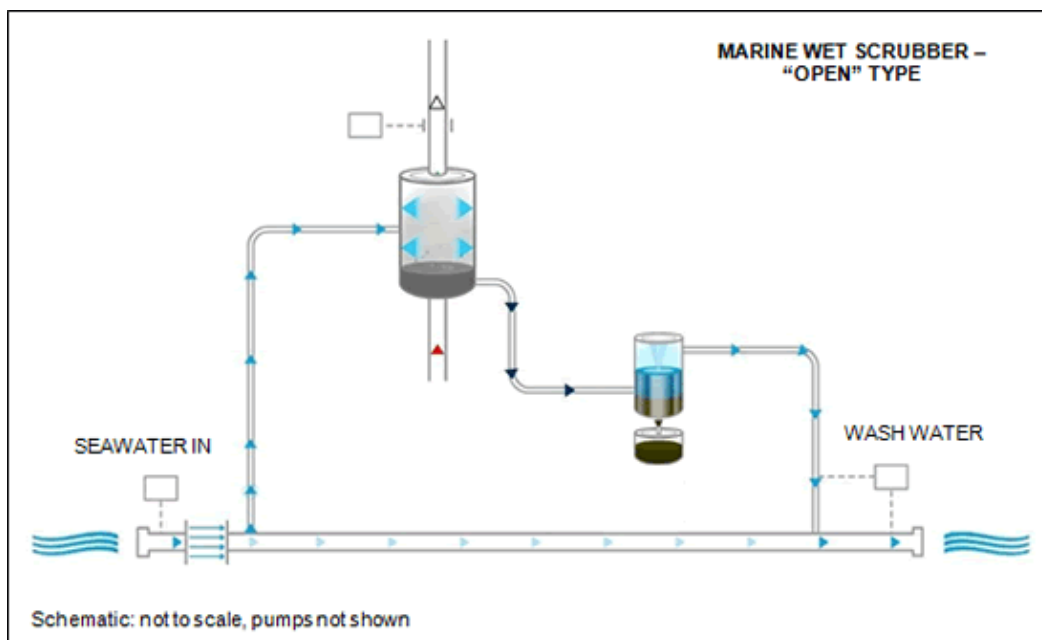
**Figure 2. The EcoSilencer<sup>®</sup> Scrubber Installed on the *Pride of Kent***

## 2.1 SEAWATER SCRUBBERS

In a seawater or “open” type scrubber (see Figure 3), seawater is used as wash water for scrubbing, and the resulting wastewater is treated and discharged back to sea. The natural alkalinity of the seawater is used to neutralize the acidity that results from SO<sub>x</sub> removal.<sup>2</sup>

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<sup>2</sup> Alkalinity in the open ocean is typically 2,200 to 2,300  $\mu\text{mol CaCO}_3/\text{L}$  (Hassellöv and Turner, 2007). Alkalinity in some coastal areas, ports, rivers and estuaries can be affected by the different drainage areas of the inflowing rivers, resulting in large variations in the chemistry. Rivers running through soil rich in carbonates will be high in alkalinity. For example, the southern rivers of the Baltic Sea run through calcite bedrock resulting in high carbonate concentrations with consequently high alkalinity (approximately 1,650 -1,950  $\mu\text{mol/L}$ ), whereas the northern rivers run through granite bedrock resulting in low alkalinity (approximately 800-1,300  $\mu\text{mol/L}$ ) (Hassellöv and Turner, 2007). In general, the alkalinity in the Baltic Sea is lower than the open sea because of the minimal exchange of water through the Danish straits. Seawater scrubbers can operate at low alkalinity levels, but in some cases the SO<sub>2</sub> removal efficiency may be reduced (Henriksson, 2007).



Source: EGCSA. 2010

**Figure 3. Open Type Wet Scrubber**

Typically, seawater systems use 45 m<sup>3</sup> of washwater per megawatt-hour<sup>3</sup> (MWh) for scrubbing (MEPC, 2008). Seawater scrubbing of the exhaust from a representative 10 MWh engine would generate 450 m<sup>3</sup>/hr or 2.8 million gallons per day (MGD) of washwater effluent. The volume of washwater required for a given scrubbing efficiency increases with elevated alkalinity and with higher water temperature (DNV, 2009). The energy consumption of a seawater scrubber is 2 to 3 percent of the engine power output (Filancia, 2009).

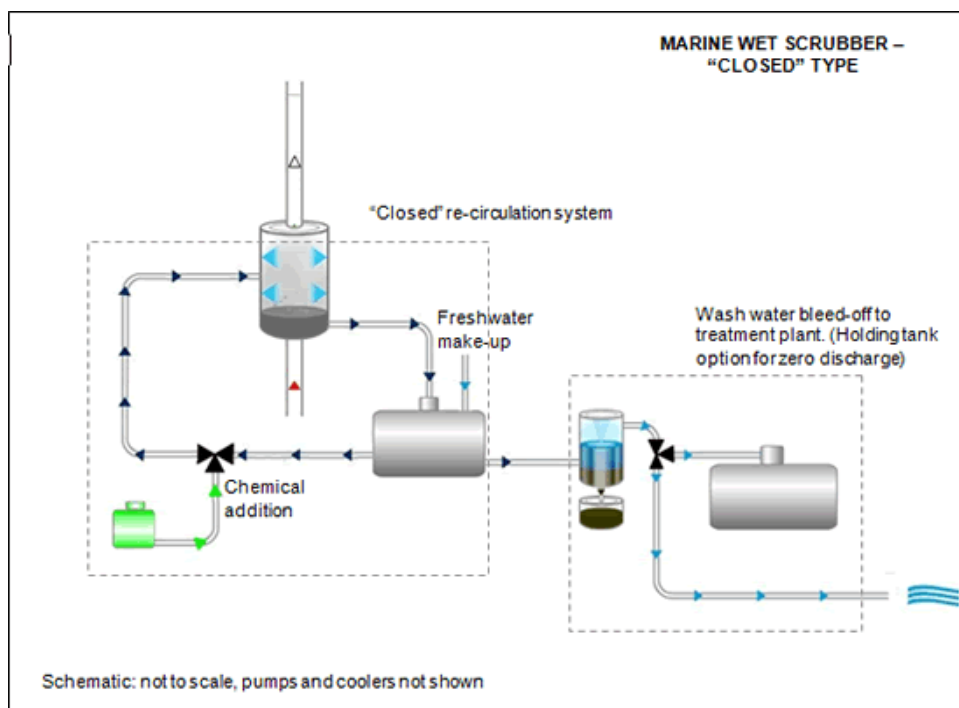
Seawater scrubbing requires the exhaust gases to be mixed with seawater to dissolve the sulfur oxides. Manufacturers use various techniques to achieve mixing without unduly obstructing the passage of exhaust gas, which could result in a “back pressure” outside of the engine builder’s limits and adversely affect engine operation. The sulfur oxides of engine exhausts typically consist of approximately 95 percent SO<sub>2</sub> and 5 percent SO<sub>3</sub> (EGCSA, 2010). When dissolved, a reaction occurs whereby the sulfur dioxide is ionized to bisulfite and sulfite, which is then readily oxidized to sulfate in seawater containing oxygen (Hassellöv and Turner, 2007).

The ionization to bisulfite and sulfite and the sulfuric acid formed from sulfur trioxide produces acidity (Karle and Turner, 2007). The acidity is neutralized initially by the alkalinity of the seawater, due to its natural bicarbonate content. After the initial buffering capacity is consumed, the pH of washwater is reduced to approximately 3. At low pH, the ionization of sulfur to sulfite is negligible and exhaust gas cleaning is limited (EGCSA, 2010).

<sup>3</sup> Maximum continuous rating (MCR) or 80% of the power rating of the fuel oil combustion unit.

## 2.2 FRESHWATER SCRUBBERS

In a freshwater or “closed” type scrubber, freshwater treated with an alkaline chemical such as caustic soda is used for neutralization and scrubbing. As shown in Figure 4, washwater is recirculated and any evaporative loss is replaced with additional freshwater. A small quantity of the washwater is bled off to a treatment plant and then discharged. Typically, closed freshwater systems have much smaller discharge rates than seawater scrubbers (approximately 0.1 to 0.3 m<sup>3</sup>/MWh) and treat a smaller volume of effluent (MEPC, 2008). Closed freshwater systems can periodically be operated in a “zero discharge mode” without discharging any washwater overboard (SSG, 2007).



Source: EGCSA. 2010

**Figure 4. Closed Type Wet Scrubber**

Freshwater scrubbers are used when high efficiency cleaning is needed or when the variable alkalinity associated with seawater precludes use of seawater scrubbers. The ability to operate an EGCS without discharging washwater for short periods of time, using available holding tank capacity, may be advantageous in water bodies that are especially sensitive or vulnerable, such as enclosed water bodies and/or those with low alkalinity. The SO<sub>x</sub> exhaust gas removal efficiency of a freshwater scrubber is typically greater than 90 percent and removal efficiencies as high as 97 percent can be obtained for exhaust from generator engines. The energy consumption of freshwater scrubbers is reported to be about 0.5 percent of the engine power output (Hatley, 2010).

### 2.3 HYBRID AND DRY SCRUBBERS

Hybrid scrubbers can operate using either seawater or freshwater as source water, while dry scrubbers operate using chemisorption. Hybrid systems can operate in either an open loop (seawater) at sea or closed loop (freshwater) in harbors, estuaries, and other sensitive water bodies (Aalborg, 2010). The advantages of a hybrid EGCS include the ability to operate in either freshwater or seawater and the ability to maintain scrubber efficiency in low alkalinity water bodies, such as the Baltic Sea, estuaries and rivers. A hybrid scrubber was installed on the 21 MW diesel engine aboard the ferry *Tor Ficaria*. The *Tor Ficaria*'s scrubber has operated over 1,000 hours since May 2010 and is reported to be the largest EGCS installed onboard a ship (Aalborg, 2010).

Dry scrubbers use solid media rather than washwater to capture sulfur oxides from the exhaust gas. Exhaust gas in a dry scrubber is passed through a bed of granular solid media, such as calcium carbonate ( $\text{CaCO}_3$ ), burnt lime ( $\text{CaO}$ ), or hydrated lime ( $\text{Ca}(\text{OH})_2$ ), to which the sulfur oxides absorb and react to form gypsum ( $\text{CaSO}_4$ ) (Couple Systems, 2010). The advantage of dry scrubbing technology is that pollutants are not transferred from air to water, as they are in wet scrubbers, but instead react with the solid media to form a byproduct. The byproduct can be reused for high-temperature desulfurization at power plants, as a raw material for cement and steel making, or as fertilizer (Couple Systems, 2010). There are over 500 dry scrubber installations for exhaust gas capture at power plants. A dry scrubber was installed to clean the exhaust gas from the 3.6 MW main engine aboard the German cellulose freighter MS *Timbus* in 2009.

## SECTION 3

# EXHAUST GAS SCRUBBER WASHWATER TREATMENT

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Operating or cleaning a wet exhaust gas scrubber for marine diesel engines and boilers generates effluent (washwater) that must be treated prior to discharge. Washwater contains gaseous and particulate emissions removed from the exhaust in the funnel by the scrubber. The SO<sub>x</sub> and nitrogen oxides (NO<sub>x</sub>) dissolved in the scrubber washwater react to form sulfuric and nitric acids, which significantly reduce the pH of the washwater leaving the scrubber. Washwater constituents can also include PM emissions captured by the scrubbers, as well as traces of oil, PAHs, heavy metals and nitrate.

Washwater effluent from seawater systems is treated, blended with reaction water to neutralize the pH, and discharged overboard. For freshwater scrubbers, only a fraction (e.g., 10 percent) of the washwater is bled off for treatment and discharged. Alternatively, freshwater scrubber washwater can be routed to a bilge water tank not destined for discharge or other suitable holding tank for treatment and discharge, or for disposal shoreside.

Treatment of scrubber washwater normally consists of suspended solids removal and pH neutralization. In current marine EGCS installations, such as the scrubbers aboard the *Pride of Kent* and *Zaandam*, the washwater leaving the scrubbers is passed through a multicyclone, a prefiltration device that predominantly separates particles larger than 30-40 µm from the washwater using centrifugal force (WATERCO, 2010). The solids from the multicyclone are collected and concentrated in a sludge tank. The amount of sludge generated by washwater treatment depends on the amount of solids captured and the water content of the sludge following settling. Solids generation for a seawater scrubber system are approximately 0.6 percent by weight of residual fuel consumed (EGCSA, 2010).

The effectiveness of centrifugal separation and settling depends on the particle size distribution and particle density (USEPA, 2009a). Additional treatment processes can be added to improve the efficiency of solids removal, including various filtration methods and/or coagulation and flocculation. Coagulation and flocculation remove particles too small for gravitational settling by aggregating them into large, more readily separable particles. Such additional treatment has been used to treat the washwater bled from closed freshwater scrubbers, such as the EGCS installed on the *Suula*.

After the washwater is treated to remove solids, it is blended with reaction water, typically seawater used for engine cooling (EGCSA, 2010). The function of the reaction water is to neutralize the pH of the washwater prior to discharge overboard. Reaction water and washwater can be mixed in nearly equal proportions, although increasing the proportion of reaction water can improve the neutralization of the acidic washwater (HA & H-K, 2010).

## SECTION 4

# IMO GUIDELINES FOR EGCSs, WASHWATER MONITORING AND DISCHARGE CRITERIA

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On October 9<sup>th</sup>, 2008, the 168 member states of the International Maritime Organization (IMO) adopted more stringent standards to control exhaust emissions from the engines that power ocean going vessels. The engine and fuel standards are included in amendments to Annex VI of MARPOL. The revised Annex VI entered into force on July 1, 2010. The sulfur content of fuel decreased in the ECAs, including the Baltic Sea, the North Sea and the English Channel, from 1.5 percent to 1 percent in July of 2010 and will decrease to 0.1 percent in January of 2015. A North American ECA (including waters adjacent to the Pacific, Atlantic and Gulf coasts and the 8 main Hawaiian Islands) will become enforceable in 2012 (USEPA, 2010b). Globally, the highest permitted sulfur content of fuel will fall from 4.5 to 3.5 percent in January of 2012 and to 0.5 percent in January of 2020. The IMO developed guidance criteria for the use of exhaust gas cleaning devices, such as SO<sub>x</sub> scrubbers, as an alternative to operating on low sulfur fuel. As a component of their analyses, the IMO also set scrubber washwater monitoring and discharge criteria in Section 10 of the Guidelines for EGCSs (Resolution MEPC.170(57)). The current Guidelines for EGCSs were adopted on July 17<sup>th</sup>, 2009 through Resolution MEPC.184(59), and are summarized in Sections 4.1 through 4.3 below.

### 4.1 WASHWATER MONITORING

The IMO guideline recommends pH, PAH concentration, turbidity and temperature should be continuously monitored and recorded when the EGCS is operated in ports, harbors, or estuaries. In other areas, these parameters should be continuously monitored and recorded whenever the EGCS is in operation, except for short periods of maintenance and cleaning of the equipment.

### 4.2 CONTINUOUS DISCHARGE LIMITS

#### 4.2.1 pH

The washwater pH must meet one of the following requirements and the results recorded in the vessel's EGCS Technical Manual (ETM) as applicable (Resolution MEPC.184(59)):

- The discharge washwater should have a pH of no less than 6.5 measured at the ship's overboard discharge with the exception that during maneuvering and transit, a maximum difference of 2 pH is allowed between the ship's inlet and overboard discharge; or
- During commissioning of the unit(s) after installation, the discharged washwater plume should be measured externally from the ship (at rest in a harbor) and the

discharge pH at the ship's overboard pH monitoring point will be recorded when the plume at a distance of 4 meters from the discharge point equals or exceeds a pH of 6.5. This discharge pH, which is found to achieve a minimum pH of 6.5 in the washwater plume 4 meters from the ship, will become the overboard pH discharge limit.

#### 4.2.2 **PAHs**

The maximum continuous PAH concentration in the discharged washwater should not be greater than 50 µg/L phenanthrene equivalence (PAHphe) above the inlet water PAH concentration. For the purposes of this criteria, the PAH concentration in the washwater should be measured downstream of the water treatment equipment but upstream of any washwater dilution or other reactant dosing unit, if used, prior to discharge. The 50 µg/L limit is normalized for a washwater flow rate through the EGCS unit of 45 tons/MWh. This limit should be adjusted for washwater flow rates, as shown in Table 1.

**Table 1. PAH Discharge Concentration Limit by Flow Rate**

Flow Rate (t/MWh)	Discharge Concentration Limit (µg/L PAHphe equivalents)	Measurement Technology
0 - 1	2250	Ultraviolet Light
2.5	900	Ultraviolet Light
5	450	Fluorescence <sup>a</sup>
11.25	200	Fluorescence <sup>a</sup>
22.5	100	Fluorescence <sup>a</sup>
45	50	Fluorescence <sup>a</sup>
90	25	Fluorescence <sup>a</sup>

Source: Resolution MEPC.184(59)

a. Fluorescence technology should be used for any flow rate > 2.5 t/MWh.

For a 15-minute period in any 12-hour period, the continuous PAHphe concentration limit may exceed the limit described above by up to 100 percent, to allow for an abnormal start up of the EGCS (Resolution MEPC.184(59)).

#### 4.2.3 **Turbidity/Suspended Particulate Matter (Solids)**

The washwater treatment system should be designed to minimize suspended PM, including heavy metals and ash. The maximum continuous turbidity in washwater should not be greater than 25 formazin nephelometric units (FNU) or 25 nephelometric turbidity units (NTU) or equivalent units, above the inlet water turbidity. However, during periods of high inlet turbidity, the precision of the measurement device and the time lapse between inlet measurement and



discharge measurement are such that the use of a difference limit is unreliable. Therefore, all turbidity difference readings should be a rolling average over a 15-minute period to a maximum of 25 FNU. For the purposes of this criteria, the turbidity in the washwater should be measured downstream of the water treatment equipment but upstream of washwater dilution (or other reactant dosing) prior to discharge. For a 15-minute period in any 12-hour period, the continuous turbidity discharge limit may be exceeded by 20 percent (Resolution MEPC.184(59)).

### **4.3 OTHER DISCHARGE LIMITS**

#### **4.3.1 Nitrates**

The washwater treatment system should prevent the discharge of nitrates beyond that associated with a 12 percent removal of NO<sub>x</sub> from the exhaust, or beyond 60 mg/L (1 mM) normalized for a washwater discharge rate of 45 t/MWh (similar to the adjustment tabulated above for PAHs), whichever is greater. All systems should be tested for nitrates in the discharge water.

#### **4.3.2 Washwater Additives and Other Substances**

An assessment of the washwater is required for those EGCS technologies which make use of chemicals, additives, preparations or create relevant chemicals *in situ*.

#### **4.3.3 Washwater Residue**

Residues (sludge) generated by the EGCS should be delivered shoreside to adequate reception facilities. Such residues should not be discharged to the sea nor incinerated onboard.

### **4.4 PERIODIC MONITORING**

The IMO washwater discharge criteria are intended to act as initial guidance for implementing EGCS designs. The IMO Guidelines state that the criteria should be revised in the future as more data become available on the contents of the discharge and its effects, taking into account any advice given by the Group of Experts on the Scientific Aspects of Marine Environmental Protection (GESAMP). Administrations (i.e., signature nations) should therefore provide for collection of relevant data. To this end, IMO requests ship owners, in conjunction with the EGCS manufacturer, to sample inlet water (for background), water after the scrubber (but before any treatment system) and discharge water and to analyze these samples using EPA or ISO test procedures for the following parameters (Resolution MEPC.184(59)):

- pH;
- PAH and oil (detailed GC-MS analysis);
- Nitrate and nitrite; and
- Metals (Cd, Cu, Ni, Pb, Zn, As, Cr and V).

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## SECTION 5

# CHARACTERIZATION OF POLLUTANTS IN EGCS WASHWATER DISCHARGES

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Prototype SO<sub>x</sub> scrubbers have been installed onboard three large ocean-going vessels: the *Zaandam*, the *Pride of Kent*, and the *Suula* (USEPA, 2009a). The scrubber trials aboard these vessels also provided data to characterize constituent concentrations in washwater discharges. These data represent the best available information regarding pollutant concentrations that can be expected in scrubber washwater discharges, including:

- pH,
- Temperature,
- Turbidity,
- Nutrients,
- Metals, and
- PAHs.

The results from the scrubber trials (summarized below) are published as project reports, which have not been peer reviewed. Samples were analyzed by certified laboratories or by academic institutions.

### 5.1 THE MS *ZAANDAM* SEAWATER SCRUBBER TRIALS

In November 2006, the Puget Sound Clean Air Agency received funding from the EPA to evaluate whether a seawater scrubbing system could be successfully designed, installed/retrofitted and operated within the tight confines of an existing cruise ship. In April 2007, Holland America Line installed a seawater scrubber in the stack of one of the five 9 MW diesel generators on the cruise ship MS *Zaandam* when she was in drydock in Victoria, Canada (HA & H-K, 2010).

The study was designed to answer a number of basic questions about seawater scrubbing, including:

- How much washwater is generated by this scrubber?
- What pollutants are present in the washwater discharge and what are their concentrations or values?
- How are these pollutants dissipated into the environment when the ship is at dock?
- How much sludge is generated by this scrubber (in grams per ton of fuel burned)?
- What are the pollutants that end up in the sludge and what are their concentrations?

Both continuous and periodic sampling of washwater was conducted onboard the *Zaandam*. In-line monitoring occurred nearly continuously between August 2007 and January 2008, and during scrubber operations between February and September 2008 and in February 2009. During these periods, the *Zaandam* operated in the Pacific Ocean, including coastal waters of Alaska, British Columbia, California, and Hawaii. Periodic samples were also collected as follows:

- August 18, 2007 - Skagway, Alaska
- August 24, 2007 - Juneau, Alaska
- September 12, 2007 - Vancouver, British Columbia
- August 30, 2008 - Vancouver, British Columbia
- September 3, 2008 - Juneau, Alaska
- September 4, 2008 - Skagway, Alaska.

Washwater sample collection followed the procedures from the Environmental Impact Assessment work performed on the ferry the *Pride of Kent* by Newcastle University and the Terramare Institute. Samples of raw seawater and scrubber washwater were collected at the inlet and discharge of the system, respectively, to assess the changes that occurred as a result of scrubbing. Samples were analyzed by certified laboratories in the jurisdictions where they were collected.

The average washwater flow rate during the scrubber trials aboard the *Zaandam* was 390 m<sup>3</sup>/hr (2.5 MGD). The following is a summary of the pollutant concentrations and other parameters measured in the raw seawater intake and the washwater samples, based upon the presentation of data in Appendix F of the final project report to EPA (HA & H-K, 2010).

### pH

The washwater discharge pH was approximately 2 standard units lower than the intake. The mean pH measured in the washwater discharged in coastal waters of California and Hawaii in 2008 was 5.8; the minimum measured value was 5.4. Over this period, it was noted that problems with pumps reduced the flow rates in the scrubber system. Higher discharge pH values were measured in Alaskan coastal waters in 2008; the mean discharge pH was 6.3. The increase in pH was achieved by raising the volume of reaction water being blended with washwater and lower engine loads (HA & H-K, 2010).

### Temperature

The increase in washwater temperature between the inlet and the discharge was less than 3.5°C throughout the duration of the project (HA & H-K, 2010).

### Turbidity

In-line continuous measurement of turbidity was found to be unreliable as air bubbles in the washwater interfered with the function of the turbidity probe. Results from periodic (discrete) sampling in 2007 indicated that turbidity and total suspended solids (TSS) decreased in concentration between the intake and the discharge. Maximum turbidity in the discharge was 8 NTUs, and the maximum change between intake and discharge was -9 percent (HA & H-K, 2010).

### Dissolved Oxygen (DO)

DO concentration in the discharge ranged from 4.0 mg/L in the warmer waters off California and Hawaii to 10.0 mg/L in the colder waters of Alaska. Although these concentrations represent varying degrees of saturation, they also suggest that re-oxygenation of washwater prior to overboard discharge was generally successful (HA & H-K, 2010).

### Alkalinity

As expected, alkalinity decreased between the seawater inlet and the washwater discharge as carbonates and bicarbonates were consumed during scrubbing. Alkalinity was reduced between 76 to 98 percent with a minimum alkalinity measured in the discharge of 21 mg CaCO<sub>3</sub>/L (HA & H-K, 2010).

### Chemical Oxygen Demand (COD)

COD generally increased between inlet and discharge as a result of the presence of sulfites in the discharge. COD increased between the discharge and the intake between 33 and 91 percent with a maximum concentration in the discharge of 130 mg/L (HA & H-K, 2010).

### Conductivity

There was no clear trend of increasing or decreasing conductivity between the inlet and discharge. The scrubber did not add new salts into the marine environment (HA & H-K, 2010).

### Total Suspended Solids

TSS decreased between inlet and discharge samples. In 2007, the maximum TSS in the discharge was 17 mg/L, and the maximum change was -73 percent. Results of periodic sampling in 2008 indicated no consistent trend for TSS between inlet and discharge samples (HA & H-K, 2010).

### Ammonia, Nitrate/Nitrite, Kjeldhal Nitrogen

According to the project report (HA & H-K, 2010), the scrubber installed aboard the *Zaandam* did not remove NO<sub>x</sub> from engine emissions. For the most part, nitrogen compounds (ammonia, nitrite/nitrate and total Kjeldahl nitrogen (TKN)) were not detected in the washwater of this EGCS. Nitrite/nitrate was measured in the washwater discharge in Skagway at a concentration of 146 µg/L, while a TKN concentration of 45 µg/L was measured in the discharge sampled in Vancouver (HA & H-K, 2010).

### Sulfites

Sulfites (compounds containing sulfide ion, SO<sub>2</sub><sup>-3</sup>) were analyzed in Alaska in 2008 using a Hach field test kit. Sulfites were not detected in the intake, but were measured in the discharge at concentrations ranging from 32 to 48.6 mg/L. These are the compounds likely contributing to the COD measured in the discharge (HA & H-K, 2010).

### PAHs

The in-line discharge probe detected PAHs at approximately 100 parts per billion (ppb, equivalent to µg/L) in California and Hawaii, and 134 ppb in Alaska. The study authors believe that the in-line measurements were not reliable as the air bubbles in the washwater interfered with the probe's ability to detect the PAHs. PAHs were not detected in any of the washwater discharge samples collected in Alaska in 2007 and analyzed by the laboratory. PAHs were detected in one discharge sample in Vancouver, at a concentration of 1.3 ppb phenanthrene equivalents (HA & H-K, 2010).

### Organic Compounds

Volatile organics were not detected in washwater discharge samples collected in 2008 (HA & H-K, 2010).

### BTEX, HEM and TPH-D/G

BTEX (benzene, toluene, ethylbenzene and xylene), hexane extractable material (HEM), and TPH-D/G (total petroleum hydrocarbon –diesel and gasoline components) were not detected in the washwater discharge (HA & H-K, 2010).

### Metals

Dissolved (filtered) and total metals concentrations were measured in 7 paired influent/effluent samples<sup>4</sup>. For several metals (arsenic, copper, lead, nickel and selenium), total

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<sup>4</sup> Data from samples collected in 2008 during tests using a flocculant chemical to treat washwater were excluded from this analysis.

and/or dissolved concentrations were measured in the washwater discharge at concentrations exceeding EPA's National Recommended Water Quality Criteria for the protection of aquatic life (NRWQC) for saltwater organisms (USEPA, 2005). In general, when exceedances were detected in the discharge, they were also detected in the intake at similar concentrations. This indicates that the ambient seawater was a likely source of the metals. Discharge concentrations exceeding the intake concentration by more than 50 percent were interpreted as a stronger indication that a metal was being added to the washwater by the scrubbing process. Details of the exceedances of water quality criteria for metals are described below and presented in Table 2 (HA & H-K, 2010):

**Table 2. Concentrations of Metals in the Washwater Discharge from the Zaandam Scrubber Trial**

<b>Metal</b>	<b>Median Total Discharge Concentration (µg/L) (n=7)</b>	<b>Median Filtered Discharge Concentration (µg/L) (n=7)</b>	<b># Samples Exceeding 150% of Intake Concentration</b>	<b>EPA NRWQC Saltwater Acute (µg/L)</b>	<b># Samples Exceeding Acute Criterion</b>	<b>EPA NRWQC Saltwater Chronic (µg/L)</b>	<b># Samples Exceeding Chronic Criterion</b>
Arsenic	81	81	1	69	6	36	7
Chromium	22	12	0	570	0	74	0
Copper	18	15	1	4.8	7	3.1	7
Lead	0.4	0.4	0	210	0	8.1	2
Nickel	20	12	5	74	2	8.2	7
Selenium	100	94	2	290	0	71	6

Source: HA & H-K. 2010

n – Number of samples

- Arsenic concentrations in all samples<sup>5</sup> (intake and discharge) exceeded acute and chronic criteria. Discharge concentrations exceeded intake concentrations in half of the samples; in one sample the total discharge concentration exceeded the intake concentration by more than 50 percent.
- All intake and discharge samples exceeded acute and chronic criteria for copper. In the majority of samples, influent copper concentrations exceeded discharge concentrations. In one sample the total effluent copper concentration exceeded the influent concentration by more than 50 percent.

<sup>5</sup> In EPA's 2009 *Study of Discharges Incidental to Normal Operation of Commercial Fishing Vessels and Other Non-Recreational Vessels Less Than 79 Feet* (USEPA, 2010), the high concentrations of chloride and other cations in seawater were found to interfere with the analytical determination of arsenic, as well as selenium. It is possible that a similar problem occurred in this study, and would explain the unexpectedly high concentrations of these metals in these samples of seawater and washwater.

- Effluent lead concentrations sampled in Juneau and Skagway in 2007 exceeded acute and chronic criteria, although the paired influent samples had similar or higher lead concentrations. Lead criteria were not exceeded in samples collected at Juneau and Skagway in 2008.
- Total and dissolved nickel effluent concentrations exceeded the chronic criterion in all samples. In two discharge samples, total nickel concentrations also exceeded the acute criterion. In 5 of 7 paired data sets, the total discharge concentration exceeded the intake concentration by more than 50 percent.
- Six total and 4 dissolved effluent samples exceeded the chronic criterion for selenium. In 2 of the sample pairs, the total discharge concentration exceeded the intake concentration by more than 50 percent.
- Washwater samples were also analyzed for antimony, beryllium, cadmium, chromium, mercury, thallium and zinc; no exceedances of water quality criteria were noted for these metals.

During operation of the seawater scrubber on the *Zaandam* in ports in Hawaii and Alaska, sooty deposits were observed rising to the surface in the washwater discharge plume, and a slight sheen was witnessed. These visible pollutants appeared to be caused from combustion-derived carbon deposits. These carbon deposits, which were nearly neutral in buoyancy, passed with the washwater through the multicyclone, attached to entrained air bubbles, and rose to the sea surface at the point of discharge. The washwater discharge contained very little petroleum hydrocarbon, but it appeared to float to the surface resulting in the slight sheen observed. The addition of an oil-water separator to the washwater treatment process ahead of the multicyclone in later trials appeared to prevent the reoccurrence of this visible soot/sheen (HA & H-K, 2010).

## 5.2 THE *PRIDE OF KENT* SEAWATER SCRUBBER TRIALS

Trials of seawater scrubbers were conducted aboard the P&O Lines *Pride of Kent*, a ferry operating between the harbors of Dover and Calais. Seawater scrubbers were installed on four 1.2 MW auxiliary engines onboard the *Pride of Kent*. The trials lasted over 16 months, during which the auxiliary engines ran almost continuously (Hufnagl et al., 2005). The ability of seawater scrubbers to reduce atmospheric emissions was examined, and the impacts of scrubber washwater discharges on the water quality in the harbors were studied. When all engines operated at full power, the washwater flow rate was 216 m<sup>3</sup>/hr (1.4 MGD). Sampling was conducted during five events held in February<sup>6</sup>, March, July, September and November of 2004, when the seawater scrubbers for the auxiliary engines were partially in use (Hufnagl et al., 2005).

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<sup>6</sup> The scrubbers were not operating during sampling in the ports of Dover and Calais in February, so data for those samples have been excluded from consideration in this document.

In each sampling event, discrete grab samples were collected at various locations in each harbor, including a transect 5 to 700 meters from the washwater discharge, at the seawater intake, and in the washwater discharge. Additional samples were collected at 6 locations throughout the seawater/washwater treatment system during the *Pride of Kent*'s crossings of the English Channel. The ambient and washwater samples were analyzed for a suite of constituents and other parameters similar to those measured on the *Zaandam*. Results from the final project report (Hufnagl et al., 2005) are summarized in Sections 0 through 0 (Hufnagl et al., 2005).

### Temperature

Washwater temperatures in the discharge were significantly higher than those measured at the seawater inlet. The temperature increases ranged from 1.9 to 4.1 °C in March and July, and from 11.9 to 16.9 °C in September and November. Discharge temperatures were greater than 37 °C (99 °F) in both ports and the channel during the September sampling event. In the July and September sampling events, a 1 °C temperature increase was measured in the ambient harbor water closest to the ship. Although the report authors expected no adverse effects to result from the discharge of heated washwater, they also noted that the buoyancy of the discharge plume resulting from the difference in temperature (and hence density) with the ambient water would have an effect on mixing in the upper water column. Note that the IMO does not provide guidelines for washwater discharge temperature (Hufnagl et al., 2005).

### pH

The SO<sub>x</sub> and NO<sub>x</sub> dissolved in the scrubber washwater form sulfuric and nitric acids, which significantly reduce the pH of the washwater leaving the scrubber. The washwater samples taken downstream from the scrubbers, prior to blending with reaction water, had low pH values, ranging from 2.67 to 3.79. The buffering capacity of seawater used as reaction water was partially effective in neutralizing the washwater acidity. The average decrease in washwater pH between inlet and discharge samples was 1.39. Discharge pH values in all of the September samples were less than 6.5, as were two-thirds of the November samples. The lowest pH measured in the overboard discharge was 6.15. These values are below the lower limit of 6.5 in the IMO Guidelines for washwater discharge, which is also the lower limit of the EPA NRWQC pH criteria for marine aquatic life. However, ambient water sampled along the discharge transects of the harbor (including directly in front of the washwater discharge at 1 to 5 m distance) indicated no observable decrease in pH (Hufnagl et al., 2005).

### Sulfate

In addition to washwater acidification, the dissolved SO<sub>x</sub> increased the sulfate concentration in the effluent. Sulfate concentrations measured in washwater downstream from the scrubber were 14 to 19 percent higher than those measured at the seawater intake. In the discharge samples, sulfate concentrations ranged between 2,600 and 3,052 mg/L, which accounts



for an increase of 0.4 to 6 percent. This may not be a significant increase, since the analytical error associated with these measurements was reported to be approximately 6 percent (Hufnagl et al., 2005).

### Nitrate

Nitrate, an important aquatic nutrient, is formed in the scrubbing process when NO<sub>x</sub> is dissolved in the washwater. In the washwater samples taken downstream from the scrubber, the nitrate concentrations were two to thirteen times higher than in the seawater inlet samples. The washwater treatment processes (multicyclone and filtration) did not reduce these concentrations because the treatment is designed to remove suspended solids and particulate pollutants, not dissolved pollutants such as nitrate. Nitrate concentrations increased between the influent and effluent discharge in 10 of 12 washwater samples. The average discharge nitrate concentration was 638 µg/L (or 144 µg NO<sub>3</sub>-N/L), 21 percent greater than the average influent concentration (Hufnagl et al., 2005).

Ammonia concentrations in washwater increased between the inlet and discharge in 4 of 10 samples; the average discharge concentration was 60 µg NH<sub>3</sub>-N/L, 5 percent higher than the average inlet concentration. Dissolved inorganic nitrogen (combined nitrite, nitrate, and ammonia) concentrations increased between the inlet and discharge in 8 of 10 samples; the average discharge concentration was 215 µg N/L, 21 percent higher than the average inlet concentration (Hufnagl et al., 2005).

### Metals

The washwater samples collected onboard the *Pride of Kent* were analyzed for total concentrations of barium, lithium, strontium, calcium, potassium and magnesium, vanadium, chromium, manganese, iron, cobalt, nickel, lead, copper, zinc and molybdenum. Copper, lead, nickel and zinc exceeded EPA's NRWQC for saltwater aquatic organisms in the washwater discharge. When exceedances were detected in the discharge, they were often also detected in the intake in similar or even higher concentrations, indicating that the ambient seawater was a likely source of the metals. In addition, the sampling conducted at several points within the washwater system onboard the *Pride of Kent* provided further identification of likely sources of the metals that were detected (Hufnagl et al., 2005).

Sampling conducted throughout the seawater/washwater treatment system revealed that the seawater scrubbing process itself did not influence the concentrations of metals in washwater. No metals, except for iron, were detected directly downstream of the scrubbers. Metals present in the washwater in particulate form, including iron and vanadium, were removed by the treatment system and retained in the sludge settling tank (Hufnagl et al., 2005).

The reduced pH of the washwater leaving the scrubber affected the solubility of metal ions. The highest metals concentrations downstream of the scrubber were measured for iron, which may be contributed by contact with the ship's steel components. Elevated copper, nickel and zinc concentrations were also detected. The copper may originate from ship coatings that contain copper as antifouling biocide while nickel, like iron, is a compound of ship steel.

Details of the exceedances of water quality criteria for metals are provided below (Hufnagl et al., 2005):

- Copper was detected in intake and discharge samples at Dover in March and November, and in November at Calais. Copper was also detected in the discharge samples collected on the channel crossing in November. All intake and discharge samples exceeded acute and chronic saltwater criteria. Intake copper concentrations ranged from 37 to 129 µg/L, while concentrations in discharges ranged from 32 to 129 µg/L.
- Lead was detected during November in discharge samples from the channel crossing and Calais, and both intake and discharge samples from Dover. Lead concentrations in these samples ranged from 18 to 34 µg/L, all of which exceeded the chronic saltwater criterion for lead.
- Nickel was detected in a single discharge sample, from Calais in November, but was not detected in the corresponding intake sample. The measured concentration, 34 µg/L, exceeded the saltwater chronic criterion.
- Zinc was detected in each of the discharge samples collected in Dover, but in only one intake sample (at one-fifth of the discharge concentration). At Calais, zinc was detected in one discharge sample. Of the samples collected during the channel crossings, zinc was detected in one intake and one discharge sample from different sampling events. All of the discharge samples exceeded the acute and chronic criteria; however, the occurrence and increase in zinc concentrations was suspected to be an artifact introduced by sample contamination.

### PAHs

Samples were analyzed for dissolved and particulate concentrations of the 16 PAHs defined to be environmentally relevant by the EPA<sup>7</sup>, including both small (4-6 rings) and large (>6 rings) PAHs. Total PAH concentrations (i.e., the sum of dissolved and particulate concentrations for the 16 PAHs) increased significantly from intake to discharge in all samples.

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<sup>7</sup> EPA's priority pollutant list of 16 PAHs includes: naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo[a]anthracene, chrysene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, dibenz(ah)anthracene, benzo[ghi]perylene, and indeno(1,2,3-cd)pyrene.

The average total PAH discharge concentration was 3,080 ng/L, twelve times the average intake concentration of 250 ng/L. The PAH composition was dominated by phenanthrene, fluorene and pyrene in all samples (Hufnagl et al., 2005).

For individual PAHs, concentrations in the washwater discharge samples were higher than concentrations measured in the seawater inlet by factors of one to two orders of magnitude.

EPA has classified seven PAH compounds as probable human carcinogens, and NRWQC have been established for nine PAHs to protect human health. A summary of the concentrations measured for these PAH compounds and for phenanthrene, the most abundant PAH in these samples, in intake seawater and washwater discharge samples is presented in Table 3. Five of the PAH compounds (benz[*a*]anthracene, benzo[*a*]pyrene, benzo[*b*] + benzo[*b*]fluoranthene and chrysene) exceed the human health criterion in all or nearly all discharge samples. Two others (dibenz[*a,h*]anthracene and indeno[1,2,3,*c,d*]pyrene) exceeded the criterion in about half of the samples (Hufnagl et al., 2005).

**Table 3. Concentrations of PAHs in the Seawater Intake and Washwater Discharge from the Pride of Kent Scrubber Trial**

PAH	Median Total Influent Concentration (ng/L) (n=13)	Median Total Discharge Concentration (ng/L) (n=13)	Dissolved Fraction, $f_d$	Human Health Criterion (Organism Consump. Only, ng/L, Except As Noted)	Number of Discharge Concentrations Exceeding Criterion
Benz[ <i>a</i> ]anthracene	6	262	0.36	18	12
Benzo[ <i>a</i> ]pyrene	5	136	0.12	18	12
Benzo[ <i>b</i> ]fluoranthene + benzo[ <i>k</i> ]fluoranthene	4	49	0.10	18	12
Chrysene	12	373	0.40	18	13
Dibenz[ <i>a,h</i> ]anthracene	8	9	0.15	18	6
Fluorene	14	137	0.97	5.3 mg/L	0
Indeno[1,2,3, <i>c,d</i> ]pyrene	5	18	0.13	18	8
Phenanthrene	54	1,230	0.88		
Pyrene	23	408	0.53	4 mg/L	0

Source: Hufnagl et al., 2005

Even higher PAH concentrations were measured inside the seawater scrubber washwater treatment system. The total PAH concentrations in samples collected prior to seawater dilution

ranged from 11,900 to 20,400 ng/L. Phenanthrene concentrations prior to seawater dilution were 5,100 to 8,200 ng/L, six to ten times lower than the 50 µg/L IMO Guideline. Most of the total PAHs were bound to soot particles, and concentrations were reduced by multicyclone treatment. Note, however, that improving the treatment efficiency would further reduce particulate PAH concentrations in the washwater discharge. The relatively high PAH concentrations in the discharge samples were predominantly the low molecular weight PAHs (such as the two and three benzene ring compounds: fluorene and phenanthrene) that are more soluble in water and not effectively removed by particle separation. Based on the average total PAH concentrations in intake and discharge samples, and assuming a washwater flow rate of 216 m<sup>3</sup>/hr and 2.25x dilution by reaction water, the EGCS on the *Pride of Kent* discharged about 33 grams of total PAH per day (Hufnagl et al., 2005).

No increase in PAH concentrations was observed in ambient harbor samples collected in front of the seawater scrubber discharge. Principal component analyses indicated that the PAH compounds measured in the seawater scrubber samples originated from a petroleum source rather than a combustion source, as would be expected from the funnel. Incomplete combustion of the fuel was suspected (Hufnagl et al., 2005).

### 5.3 THE *SUULA* FRESHWATER SCRUBBER TRIAL

In 2008 a Finnish maritime consortium installed and tested an EGCS aboard the tanker MT *Suula* (Wärtsilä, 2010). This scrubber trial offers a contrast to the other studies of seawater scrubbers because the *Suula* was outfitted with a closed freshwater scrubber. A medium speed 680 kW auxiliary engine fed exhaust gas to the scrubber, which was smaller than what would be used in a full scale EGCS. In the freshwater scrubber, sulfur oxides in the exhaust gas are transferred to washwater containing sodium hydroxide and sulfates are formed. The washwater leaving the scrubber was dosed with sodium hydroxide, cooled by a seawater heat exchanger to limit evaporative loss, and then re-circulated back to the scrubber. A fraction of the washwater was bled off for treatment and discharge, at a rate of about 0.1 m<sup>3</sup>/MWh or 0.07 m<sup>3</sup>/hr (430 gallons per day, GPD), based upon the auxiliary engine size (personal communication with Wärtsilä; see Attachment A). The bleed-off washwater was treated prior to discharge to remove pollutants in a high efficiency treatment plant that combined coagulation and flocculation, dissolved air flotation, oil and sludge skimming, and granular activated carbon adsorption (Wärtsilä, 2007). Pollutants removed from the bleed-off washwater were retained as sludge, which was collected into a residual sludge tank and held for disposal at a shore-side waste reception facility. The rate of sludge generation was approximately 0.1 to 0.4 kg/MWh (Wärtsilä, 2010).

As a part of certification tests that were conducted during the scrubber trial, water quality for the bleed-off washwater was demonstrated to the classification societies Germanischer Lloyd and Det Norske Veritas (DNV). The freshwater scrubber fulfilled all the IMO Guideline

discharge quality criteria for pH, turbidity, PAHphe, and nitrate due to the efficiency of the water treatment unit (Wärtsilä, 2010). The bleed-off treatment unit was found to have a very high cleaning efficiency regardless of the fuel sulfur content (both low- and high-sulfur content fuels were tested). Results from the project report are summarized below (Wärtsilä, 2010):

### pH

Sodium hydroxide (NaOH) was added to the scrubbing water circulation to maintain the process pH and the efficiency of SO<sub>x</sub> removal. Due to efficient NaOH dosing and monitoring in this system, the pH of the discharge was maintained at a value of 7.65 (Wärtsilä, 2010).

### Nitrate

Certification tests demonstrated that the nitrate concentration in the bleed-off discharge was less than 2,000 mg/L. When normalized for a washwater discharge rate of 45 t/MHw<sup>8</sup>, this concentration is reduced to 9 mg/L, which is below the IMO limit of 60 mg/L (Wärtsilä, 2010).

### Turbidity

The turbidity of the discharge bleed-off following water treatment was 0.5 FNU, also under the IMO limit of 25 (Wärtsilä, 2010).

### PAHs and Organic Compounds

The PAHphe concentration of the discharged bleed-off water was 14 µg/L. This is considerably lower than the flow-normalized IMO limit of 2,250 µg/L. The bleed-off treatment unit achieved PAHphe reductions of 97 to 98 percent when the scrubber was tested with fuels of different sulfur contents. Hydrocarbon (C10-C40) concentrations were also reduced by nearly 100 percent, to discharge concentrations of less than 1 mg/L (Wärtsilä, 2010).

The authors of this study noted that continuous measurement of the PAHphe equivalence in a reliable way is challenging using existing technology. Traditional sampling and laboratory analyses onshore are a more reliable approach to monitoring PAH content in discharge. Additional research and development work was suggested to find the best methodology for PAH monitoring in the discharge (Wärtsilä, 2010).

### Metals

Metals were also removed from the bleed-off washwater by the treatment unit prior to discharge. The sum of metals<sup>9</sup> specified by IMO Resolution MEPC.184(59) was reduced by 66

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<sup>8</sup> See Section 4 for an explanation of the IMO Guideline discharge limit flow normalization.

to 83 percent, to a concentration less than 60 mg/L (total metals concentration). The discharge concentrations for individual metals were not reported. The IMO Guidelines indirectly limit the permissible amount of metals in the washwater discharge by its the turbidity criterion. As this case illustrates, a considerable concentration of metals can be discharged even though the discharge turbidity is well under the limits established by the IMO Guidelines (Wärtsilä, 2010).

#### 5.4 SUMMARY OF MARINE EGCS SCRUBBER TRIALS

The trials conducted with wet scrubbers onboard marine vessels have demonstrated the capabilities of this technology to remove sulfur emissions from exhaust gas. They have also provided limited data characterizing constituent concentrations in washwater discharges. The trials aboard the *Zaandam*, *Pride of Kent* and *Suula* provided measurements of several washwater constituents including pH and pollutants removed from the exhaust gas (SO<sub>x</sub> and NO<sub>x</sub>, and the products of their transformation: acidity, SO<sub>4</sub>, NO<sub>3</sub> and COD) and PM (PAHs, hydrocarbons and metals). Neutralization of washwater was achieved by blending with sufficient seawater “reaction water”. Washwater was also treated to remove the suspended solids that were attributed to PM removed by the scrubbers. Treatment was accomplished using multicyclones alone or in combination with filtration, or, more effectively, using an advanced treatment system incorporating coagulation and filtration, flotation and adsorption.

Issues with the technology for continuous monitoring of PAHs, as required by the IMO Guidelines, were noted in two of the trials. One trial also reported difficulties with continuous monitoring of turbidity. Washwater monitoring results also suggested that some constituents warrant further consideration, including pH, metals, PAHs and nitrate (see Section 6). Although all of the constituents are addressed in the IMO scrubber washwater guidelines, the guideline limits may be inadequate for metals and PAHs.

It should also be noted that the trials aboard the *Zaandam*, *Pride of Kent* and *Suula* were limited, because the scrubbers were installed on auxiliary engines that were not always operating at full power when washwater was sampled. When exhaust is scrubbed at higher power output levels, or when larger propulsion engine exhaust is scrubbed, more washwater will be generated and discharged. Due to this and the fact that constituent concentrations in exhaust and/or washwater may be different at higher power outputs, the representativeness of the trial results may be uncertain. In addition, the performance and effects of seawater scrubbers may be different in areas with brackish water or freshwater (Hufnagl et al., 2005). Freshwater may have, for example, less pH buffering capacity, unless the water drains a carbonaceous area; therefore, the ability of such a water body to assimilate acidic washwater discharge may be limited.

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<sup>9</sup> These metals include cadmium, copper, nickel, lead, zinc, arsenic, chromium and vanadium.

## SECTION 6

# ASSESSMENT OF POLLUTANTS DISCHARGED IN SCRUBBER WASHWATER AND PROTECTIVENESS OF IMO GUIDELINES

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In Section 5, data were presented that characterize the constituent concentrations that can be expected in scrubber washwater discharges. These concentrations were compared to EPA NRWQC as a preliminary screen for all discharge data with the potential to cause or contribute to the nonattainment of a water quality standard in a given receiving water body. The pollutant concentrations were also compared to IMO Guideline limits, when available. In addition, an analysis of the protectiveness of the IMO Guideline washwater limits offered in an impact assessment prepared for the European Commission on the revision of Directive 1999/32/EC<sup>10</sup> was considered and incorporated in this discussion where appropriate (AEA, 2009).

EPA's NRWQC are recommended concentrations of analytes for a water body that are intended to protect human health, aquatic organisms and the water body uses from unacceptable effects from exposures to these pollutants. The NRWQC are not directly related to analyte discharge concentrations for a number of reasons (USEPA, 2010a). First, NRWQC are based not only on concentration, but also on duration and frequency. Second, it is not always necessary to meet all water quality criteria within the discharge pipe to protect the integrity of a water body (USEPA, 1991). Under EPA's regulations at 40 CFR 122.44(d)(1)(ii), when determining whether a discharge causes, has the reasonable potential to cause, or contributes to an in-stream excursion above a narrative or numeric criteria within a state water quality standard, the permitting authority will use procedures that account for, where appropriate, the dilution of the discharge in the receiving water. A mixing zone allows for ambient concentrations above the criteria in small areas near outfalls while dilution occurs. To ensure mixing zones do not impair the integrity of the water body, the permitting authority will determine the mixing zone such that it does not cause lethality to passing organisms and, considering likely pathways of exposure, significant human health risks.

Nevertheless, comparing analyte concentrations in vessel discharges to NRWQC provides a conservative screen of whether these discharges cause, have the reasonable potential to cause, or contribute to nonattainment of the water quality standards in a water body. If the concentration of a given analyte in vessel discharge is less than the applicable screening criterion values, the discharge would likely not cause, have the reasonable potential to cause, or contribute to nonattainment of a water quality standard based on that value, particularly after considering assimilation and/or dilution by the receiving water. On the other hand, if the concentration of a given analyte in vessel discharge is greater than the applicable screening criterion value, then there is the possibility of ecological or human health risk.

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<sup>10</sup> Sulfur Content of Certain Liquid Fuels

Because the washwater discharges were measured at the “end of pipe” before being released into a harbor where they are subsequently diluted, discharge concentrations greater than the applicable criterion do not necessarily indicate that a discharge poses a significant risk or would be likely to cause or contribute to a water quality standard exceedance. However, exceedance of a screening benchmark indicates that the discharge warrants further consideration regarding the potential to cause or contribute to nonattainment of water quality standards.

Mobile sources such as vessels complicate the analysis because they discharge into many different water bodies. In general, greater mixing and dilution would be expected for discharges from vessels that are in motion while discharging than from stationary sources. Vessel discharges to areas with high vessel traffic, areas with a low degree of flushing, or impaired water bodies could reduce mixing and dilution. With these factors in mind and assuming the discharge data presented in this document are representative of scrubber washwater discharges in general, a discharge concentration marginally above the applicable screening criterion value is most likely not of significant concern. On the other hand, a discharge concentration substantially above the applicable screening criterion value (e.g., by a factor of 10 or 100) may be more likely to be of concern, particularly if the discharge is of significant volume, is in an area of low flushing, is in an area where there is a high degree of vessel traffic, or is in a waterbody that is already impaired or under other stress.

The dispersion (mixing) of pollutants discharged from a ship has been evaluated using numerical hydrodynamic models. The overall dispersion has been modeled for different scenarios regarding ship size, washwater discharge point and speed (MARINTEK, 2006). The dispersion in the wake behind a moving vessel has been identified as the dominant dilution process (MARINTEK, 2006). For a 163 m length vessel moving at a constant speed of 14.5 knots with a washwater discharge of 440 m<sup>3</sup>/hour at 8 m depth and 20 m ahead of the stern, the washwater was diluted by a factor of 1:30 before the discharge passed the stern of the ship and by a factor 1:2,000 at a distance 50 m behind the stern. At slower vessel speeds, such as while maneuvering in a confined harbor, less dilution is expected. The power output of the propulsion engines is also expected to be lower at slower vessel speeds, which would also reduce the rate of washwater discharge (assuming the vessel is scrubbing propulsion engine exhaust).

Dilution in port may be influenced by local conditions, but much less mixing is expected in comparison to the discharge from a moving vessel. One study assumed a speed of 0 knots, a washwater temperature of 7.5°C, and an ambient current speed of 5 centimeters per second (cm/s) (MARINTEK, 2006). A dilution factor of 1:100 in the center of the plume was predicted less than 20 m downstream from the discharge, corresponding to an average dilution factor of approximately 1:150. The dilution factor will probably be smaller than this if the washwater discharge is warmer than 7.5°C (for comparison, the maximum washwater discharge temperatures measured during the *Pride of Kent* trials were 37°C), because heated effluent will be buoyant and may tend to “float” on top of the ambient water instead of mixing.



The pollutant concentrations were also compared to IMO Guideline limits, when available. The IMO washwater criteria are stipulated in Section 10 of Annex 9 of Resolution MEPC.184(59) and regard pH, PAH content, turbidity and nitrate content. These concentration limits do consider the dilution of washwater discharges in the ambient water in a mixing zone surrounding the vessel. The IMO Guideline limits also reflect the results of monitoring, which generally did not detect increases in pollutant concentrations in the discharge plume, even in close proximity to the point of discharge. The current IMO Guidelines imply that the washwater criteria apply everywhere; however, in earlier versions the criteria were only applied to harbors, estuaries and ports (AEA, 2009). It is uncertain, at present, if separate limits will be developed for operation at open sea.

## **6.1    pH**

There is some concern that sending seawater back into the ocean with acidic sulphur-containing wastewater is harmful enough to the marine ecosystem that it “renders the technology impractical” (Kehoe et al., 2010). The washwater from a seawater scrubber unit can have a pH as low as 3; therefore, to avoid a negative impact on ecosystems and potential corrosion issues, the washwater must be further neutralized and diluted with additional seawater to increase the pH level to greater than 6.5, as required under the IMO EGCS Guidelines. Alternatively, the IMO Guidelines allow the pH limit for the discharge to be determined during commissioning by measuring pH in the plume at a distance of 4 m from the discharge point, and determining the discharge pH that corresponds to a plume pH equal or exceeding a value of 6.5. This alternative compliance method of measuring the pH is consistent with EPA CORMIX principles where 4 m is considered the boundary of the initial mixing zone between water discharged overboard and water surrounding the vessel (Jirka, 1996 and EGCSA, 2010).

Low pH water can adversely impact marine organisms such as shellfish and, as many organisms are only able to survive when environmental conditions are stable, a decrease in pH may be a risk for those organisms. The IMO indicates that, in general, no environmental harm is considered to arise from short-term exposure of seawater with pH values as low as 6.5 (Hassellöv and Turner, 2007). A different pH discharge criteria is applied for moving vessels: during maneuvering and transit, a maximum difference of 2 pH units is allowed between the ship’s inlet and overboard discharge. As previously noted, for vessels underway, the mixing of discharged washwater with fresh seawater by the turbulence of the ship’s wake is highly effective, so that recovery of the pH to that of the surrounding water is rapidly achieved (EGCSA, 2010).

Most studies of the pH reduction associated with scrubber washwater discharges have focused on local receiving water impacts. As seawater scrubbing cuts short the cycle of SO<sub>2</sub> directly deposited in the ocean, this technology may also accelerate the pH decrease in surface waters of the oceans. However, this effect is minor compared to ocean acidification due to

increased carbon dioxide concentrations in the atmosphere (Kehoe et al., 2010). One study estimated that the pH of the ocean would decrease by 0.02 within the next 100 years, assuming that sulfur is evenly distributed in the 100m deep surface layer (Kehoe, 2010). In comparison, another study predicted that average pH of the surface ocean may decline by 0.255 by year 2100 (Kehoe, 2010).

EPA's NRWQC criteria for marine aquatic life is expressed as a pH in the range of 6.5 to 8.5, but not more than 0.2 standard units outside of normally occurring range (USEPA, 1976). EPA guidelines concerning the introduction of acids state that, within the initial mixing zone, the pH change is not allowed to be higher than 0.2 (EGCSA, 2010). In comparison to the EPA pH criteria, the IMO Guidelines have the same lower limit, but lack the limit on pH change.

Problems were encountered during two of the seawater scrubber trials with neutralization of the acidic washwater resulting in the discharge of washwater with pH values below 6.5. On the *Zaandam*, the discharge washwater pH was more than 2 standard units lower than the intake values. The mean pH of the discharged washwater was 5.8 while in the coastal waters of California and Hawaii and 6.3 in Alaska. The discharge of low pH washwater effluent was associated with low washwater and/or reaction water flow rates. On the *Pride of Kent*, the average decrease in washwater pH was only 1.39. However, all of the discharged washwater pH values were below 6.5 during one sampling event; two-thirds of the pH values were below this limit in another.

A 2007 study calculated the amount of water needed for scrubbing SO<sub>2</sub> and dilution to first obtain pH of 6.5 and then a pH change within the initial mixing zone of 0.2 (Hassellöv and Turner, 2007). The nominal flow rate of scrubbing water used by MEPC is around 45 t/MWh giving about 540 t/hr for a ship with a 12 MW engine. The estimated quantities of water needed for scrubbing are presented in Table 4. With the present criteria for pH, the dilution in the sea and natural buffering may rapidly achieve acceptable levels, even in confined areas. Furthermore, vessels use substantially less propulsion power when traveling at low speeds and maneuvering in harbors and other confined areas. Vessels using EGCS for propulsion engines should therefore discharge less washwater in harbors, further limiting the impact of seawater scrubbers on receiving water pH. As previously stated, operation of a seawater scrubber in brackish or freshwater may have different effects (e.g., fresh waters with less pH buffering capacity). Almost 7 times more water for dilution is needed when scrubbing takes place in freshwater, compared to the open sea.

**Table 4. Approximate Amount of Water (t/hr) Affected by a Scrubber for a 12 MW Engine**

	Quantity of Water		
	Open Ocean	Baltic Sea	Freshwater River
Water for scrubbing	700	900	2,500
Water for dilution to pH = 6.5	1,400	1,700	15,000
Factor for dilution to $\Delta$ pH of 0.2	3	3.5	2.5
Total amount of water	6,300	9,100	44,000

Source: Hassellöv and Turner, 2007

In an environmental impact assessment of the *Pride of Kent* seawater scrubber trials, samples were taken directly in front of the washwater discharge from a stationary vessel in each harbor at distances of 1 to 5 m, 50 m, 350 m and 700 m. While washwater samples taken from inside the ship had pH values of 6.2 to 6.5, in no sample taken within the discharge plume was the pH below that of the surrounding water (EGCSA, 2010).

The IMO criterion for pH limits the amount of water that may be affected by low pH during scrubber operation to a reasonable amount. This is dependent on the dilution, volume of water and the specific area of concern. As noted, specific attention may be needed for waters with low alkalinity. Increasing the volume of reaction water used to neutralize washwater in open seawater systems, or operating closed freshwater systems in zero-discharge mode as needed, may be practical solutions to limit pH change in vulnerable (i.e., low alkalinity) receiving waters.

## 6.2 PAH

PAHs are the largest known group of carcinogenic substances and include many individual chemical substances containing two or more condensed aromatic rings. PAHs occur naturally in petroleum and are also produced as by-products of fuel combustion. PAHs are an important class of environmental contaminants that are known to accumulate in ecosystems. The EPA has identified 16 PAH compounds as priority pollutants. Some of these compounds are carcinogenic and/or mutagenic to mammals; in addition, they have both acute toxicity and sub-lethal effects on some aquatic organisms. PAHs may also bioaccumulate in edible shellfish, which gives them a pathway to humans (Hartmann and Quinn, 1999).

The IMO has set limits for the online monitoring of phenanthrene, based on studies to date which have shown no negative influences of EGCS washwater on port environments. Phenanthrene is the most prevalent of the 16 EPA PAHs found in the vessel washwater systems (Behrends et al., 2005). Furthermore, the IMO asserts that, as PAHs are also found naturally in

petroleum, their monitoring ensures that unburned oil or hydrocarbons do not enter the sea (EGCSA, 2010). The IMO also requests ship owners to sample inlet and untreated and discharged washwater, and to employ gas chromatography-mass spectrometry analysis for PAHs.

Sediments can be disturbed during the maneuvering of a ship in shallow water, and as a result may enter the washwater system. Since harbor sediments are often contaminated with PAHs, PAHs can enter the washwater system along with the sediment. The IMO therefore requires the background concentration of PAH at the washwater inlet be taken into account when measuring the PAH concentration at system discharge. It is also required that washwater monitoring take place following water treatment, but before any dilution for correction of the washwater pH.

While a set of 16 PAHs is customarily analyzed and measured as individual chemicals, the IMO Guidelines set the washwater criteria for PAH in phenanthrene equivalents. The rationale for this is unclear but may be that measuring PAH is a surrogate for hydrocarbons and phenanthrene was found to be the most abundant PAH in the analysis of washwater during trials on the *Pride of Kent*. However, the concept of phenanthrene equivalents is not well established and needs to be explained or replaced (AEA, 2009). Assuming that it simply means that the phenanthrene concentration is measured, the 50 µg/L criteria correspond to about 2.2 g/MWh of PAHphe. Thus, the washwater criterion may be high, especially considering that the scrubber washwater should be treated before monitoring for PAHphe. A 12 MW engine could, with the suggested limit, emit around 27 g/hr phenanthrene in addition to unknown amounts of other PAHs. This emission limit may be unacceptably high, and widespread use of scrubbers emitting washwater with PAH concentrations close to this limit could pose a risk to the environment (AEA, 2009).

The Oslo and Paris Conventions for the protection of the marine environment of the northeast Atlantic (OSPAR) have developed Ecotoxicological Assessment Criteria (EAC) for a large range of chemicals, including PAHs. The EAC can be applied as Predicted No Effect Concentration (PNEC) values (MARENTEK, 2006). The EAC for phenanthrene in water is proposed as a range: 0.5 to 5 µg/L (provisional value). The PNEC value is the maximum permissible concentration that can be sustained over time. The Predicted Environmental Concentration (PEC) equals the proposed washwater criteria multiplied by the dilution (if inlet concentration is assumed to be zero). Since the washwater criterion is set to 50 µg/L PAHphe (for a scrubber washwater flow of 45 t/MWh), the washwater must be diluted by a factor of 10 to 100 to reach this PNEC concentration (AEA, 2009). Furthermore, the background concentration should also be considered, which may lead to further limits on the emissions.

The median concentration of phenanthrene measured in the washwater following treatment but before mixing with reaction water on the *Pride of Kent* was 6.1 µg/L, well below

the 50 µg/L PAHphe IMO Guideline limit. Comparison of the other PAHs measured in washwater discharged by the *Pride of Kent* during scrubber trials to the EPA NRWQCs suggests that scrubbers may emit washwater with concentrations of other PAHs that could pose a risk to the environment. The EGCS on the *Pride of Kent* was discharging about 33 grams of total PAH per day. Dividing the median discharge concentrations by the applicable human health criteria (values tabulated in Section 5), the dilution required to reach the criteria is calculated to be as high as 21 for chrysene, 15 for benz(a)anthracene, and 7 for benzo(a)pyrene. Phenanthrene concentrations measured in the washwater discharge on the *Zaandam* and *Suula* were <1.3 µg/L and 14 µg/L; concentrations for the other PAHs were not reported.

The PAH criterion appears to have been selected to allow continuous monitoring of the washwater discharge. While it may be appropriate to use phenanthrene for monitoring purposes, the criteria should, nevertheless, ensure that all of the environmentally relevant PAHs are controlled. How the measured phenanthrene equivalents relates to the 16 EPA PAHs, for example, or its correlation to total hydrocarbons needs to be established during certification. Furthermore, it remains to be established that the PAH IMO Guideline limit will ensure that the levels of total hydrocarbon compound emissions are at safe levels (AEA, 2009).

### 6.3 TURBIDITY

Turbidity is a measure of the amount of suspended solids in the water, based upon the loss of optical transparency (i.e., cloudiness) of the water. When combined with PAH, the measurement of turbidity is intended to demonstrate that the scrubber and washwater treatment system is operating correctly (EGCSA, 2010). However, this method of continuous monitoring has not been demonstrated to be a reliable measure of the concentration of PM (including metals) emitted with the washwater (AEA, 2009). Turbidity can be a useful indicator of the status of the scrubber (i.e., that suspended particles are not being formed in the scrubbing process and/or the washwater treatment process is functioning properly). Turbidity, however, is not a direct method of determining the amount of exhaust particles that end up in the washwater because there is no direct correlation between turbidity and particle concentration. Further, turbidity values are strongly dependent on the size of particles in the water; smaller particles are likely to have significantly less influence on the measured turbidity than larger ones. Studies are required to correlate the turbidity measurements with concentrations of PM, ash, metals, etc. in the washwater before turbidity can be considered as a reliable indicator of particulate levels in the washwater (AEA, 2009). These uncertainties make it difficult to make an environmental assessment of the turbidity criteria.

Turbidity was measured in the scrubber trials onboard the *Zaandam* and the *Suula*. During the *Zaandam* trials, the maximum turbidity was 8 NTUs, well below the 50 NTU IMO Guideline limit. Turbidity levels actually declined between the inlet and discharge in the first

year of that trial (i.e., the scrubber system removed turbidity from the seawater used as scrubber washwater). On the *Suula*, the turbidity was 0.5 FNU, also well below the guideline limit.

#### 6.4 NITRATE

Nitrate is the most highly oxidized form of nitrogen, and excess nitrate concentrations in aquatic systems can result in a rapid increase or accumulation in the population of algae, possibly leading to algae blooms and eutrophication. This can disrupt functioning of an aquatic system, causing a variety of problems such as a lack of oxygen in the water needed for fish and shellfish to survive (Behrends and Liebezeit, 2003). In near-shore or harbor situations, where phosphorous is available (e.g. from river inputs, runoff from agriculture or direct input of domestic sewage), addition of nitrates may lead to enhanced biomass production.

The IMO Guidelines include two criteria for nitrate concentration in the washwater: 60 mg/L or a limit based on removing 12 percent of the NO<sub>x</sub> from the exhaust stream, based on a hypothetical scrubber design capable of removing more NO<sub>x</sub> than the soluble NO<sub>2</sub> fraction. A scrubber unit on a ship operating close to this 12 percent limit may, depending on the sea area, increase the ship's contribution to the nitrate load in the sea (AEA, 2009). In principle, washwater discharges from numerous ships operating EGCS could lead to large additional loadings of nitrates to sensitive aquatic ecosystems.

A 2009 report analyzed the impact of the 12 percent exhaust NO<sub>x</sub> removal criteria in the Baltic Sea (AEA, 2009). The Baltic is heavily trafficked by vessels, is a SECA, and is highly impacted by eutrophication. Serious efforts have been made to decrease the flow of nutrients into the Baltic and the total emission of NO<sub>x</sub> from shipping in the Baltic is currently around 400 kilotons per year. Modeling was used to estimate that about 13 percent of the NO<sub>x</sub> emitted from shipping in the Baltic Sea is also deposited in that water body; the rest is deposited over land or (to a smaller extent) in other sea regions. Consequently, approximately 107 kilotons per year (calculated as nitrates) is deposited in the Baltic Sea from Baltic shipping. If all of these ships were to use scrubbers, and all of these scrubbers captured 12 percent of the NO<sub>x</sub> in the exhaust and released it as nitrates in the scrubber washwater, the total nitrate loading from vessels would increase to 193 kilotons (an increase of about 86 kilotons per year). Notwithstanding several unrealistic assumptions, this estimate does give a maximum possible increase in nitrate loading. Twenty-five percent of the total load of nitrogen to the Baltic Sea comes from atmospheric deposition; the rest comes from rivers and direct waterborne discharges. Thus, the hypothetical maximum increase in the load of nitrates to a water body of the size of the Baltic Sea would be a nearly-negligible, 2 percent, if all ships were to use scrubbers.

A 2009 report estimated the potential for additional biomass production due to the discharge of nitrate from the washwater of an EGCS, using the nitrate levels monitored over the ten-month period of the *Pride of Kent* trials (Hufnagl, 2005). Adding 9.59 µM of nitrate to the 10-60 µM ambient concentrations measured in harbors, when converted by stoichiometry, equals

an increase in plankton biomass of 2.13 mg/L over the 2.2-13.3 mg/L biomass produced by ambient nutrients. The potential for increase in annual production was equated to less than the actual production during one sunny day (Hufnagl, 2005). Thus, these calculations also demonstrate that the impact of the nitrates discharged in washwater from seawater scrubbers is likely to be minimal (EGCSA, 2010).

Nitrate concentrations were measured in all three of the scrubber trials. Low nitrate concentrations ( $>146 \mu\text{g/L}$  and  $638 \mu\text{g/L}$ ) were measured in the *Zaandam* and the *Pride of Kent* washwater discharge. Onboard the *Suula*, a significantly higher concentration ( $<2,000 \text{ mg/L}$ ) was detected. However, since the IMO Guideline limit of  $60 \text{ mg/L}$  for nitrate is normalized by the washwater discharge rate, the normalized nitrate concentration of  $9 \text{ mg/L}$  is below the IMO Guideline (the *Suula*, using a closed scrubber system, discharges bleed-off washwater at about  $1/500^{\text{th}}$  of the customary rate for an open seawater scrubber).

Nitrate loadings from washwater discharges can be calculated from the *Pride of Kent* and *Suula* EGCS trial data. Based on the average concentration increases between intake and discharge samples, the nitrate washwater loading from the seawater scrubber EGCS on the *Pride of Kent* was  $0.35 \text{ kg NO}_3\text{-N}$  per day. The dissolved inorganic nitrogen washwater loading was  $0.53 \text{ kg N/d}$ . The freshwater scrubber aboard the *Suula* generated a nitrate loading of less than  $3.4 \text{ kg NO}_3\text{-N}$  per day.

## 6.5 SULFATE, COD AND DISSOLVED OXYGEN

Sulfate is an abundant and conservative component of seawater; therefore, the discharge of this parameter does not represent a limiting factor for seawater scrubbing. Studies and field testing confirm that the sulfate increase from exhaust gas scrubbing would be insignificant when compared with the quantity already in the oceans (Hassellöv and Turner, 2007 and Hufnagl, 2005). For example, washwater sampling aboard the *Pride of Kent* demonstrated that scrubbers added a negligible amount of sulfate.

When  $\text{SO}_2$  is dissolved in water, a reaction occurs whereby the sulfur dioxide is ionized to bisulfite and sulfite, which is then readily oxidized to sulfate in seawater containing oxygen (Hassellöv and Turner, 2007). This process increases the COD, which could potentially have an adverse impact on aquatic systems. COD is a measure of the theoretical oxygen consumption of a water sample (i.e., the amount of oxygen required for degradation of the organic matter). There are no environmental standards for COD (MARINTEK, 2006).

Tolerance to reduced dissolved oxygen varies between organisms, life stages and environmental conditions. The Norwegian Marine Technology Research Institute concluded that COD was not a matter of concern under the circumstances of their study (MARINTEK, 2006). Using worse case scenarios, a study evaluated how much dilution of washwater would be required to return oxygen levels to within 1 percent of those of the ambient water. They found

that if the pH of the washwater had already been corrected to within 0.2 standard units of ambient values, then no further dilution would generally be required to maintain DO levels (Hassellöv and Turner, 2007)

It is known from various in-field tests and modeling of discharge plumes that the pH and oxygen of discharged water very rapidly returns to that of the surrounding water, especially when the vessels is underway; thus, the IMO does not require dissolved oxygen to be monitored (EGCSA, 2010).

## **6.6 METALS**

Metals are a diverse group of pollutants, many of which are toxic to aquatic life and humans. While some metals, including copper, nickel, and zinc, are known to be essential to organism function, many others, including thallium and arsenic, are nonessential and/or are known to have only adverse impacts. Even essential metals can do serious damage to organism function in sufficiently elevated concentrations. Adverse impacts can include impaired organ function, impaired reproduction, birth defects, and at extreme concentrations, acute mortality.

There are a number of sources for metals to enter the washwater in wet scrubber systems:

- System materials, typically iron, copper and zinc may be a source of metals. The reduced pH of washwater, which can be as low as pH 3 within the system, will increase the solubility of metal ions and therefore the choice of materials is very carefully considered by exhaust gas cleaning system designers.
- System inlet water may contain metals found in seawater or from electrochemical protection to prevent fouling of seawater pipes and from antifouling paints (typically copper). Electrochemical protection is often installed at the inlet to seawater pumping systems to prevent the parasitic growth of organisms that may foul pipework, filters and coolers of ship's machinery. An EGCS may take a washwater supply from a point with electrochemical protection, but will not have a direct influence on it (EGCSA, 2010).
- The combustion of fuel and lubricant is another source of metals, typically vanadium, nickel, calcium and zinc. Although it makes up a relatively small amount of the overall PM, ash represents the incombustible residue of burning fuel oil and lubricant. The majority of fuel oil ash content consists of metal compounds that occur naturally in petroleum; principally vanadium and nickel, which are oil soluble and so cannot be removed by onboard pre-treatment such as filtration and centrifugal purification (EGCSA, 2010). These metals can also enter ecosystems from unscrubbed exhaust emissions into the atmosphere.

The IMO Guidelines do not contain any limits for the concentrations of metals in washwater discharge, although the IMO requests ship owners to sample and analyze washwater for a suite of metals. Turbidity is monitored as a surrogate for suspended solids. Presumably,



turbidity values below the limit of 5 FTU/NTU indicate that the washwater treatment system is effectively removing particulates from the washwater, as well as particulate metals. Washwater samples taken from various points within the scrubber system during the *Pride of Kent* trials showed that the majority of metals were bound to particles or were particulates themselves and were effectively removed by the washwater treatment plant.

Monitoring conducted during scrubber trials demonstrates that metals are present at concentrations above EPA NRWQC for several metals, even though the washwater treatment plants were functioning and turbidity limits were being met. The monitoring during scrubber trials also considered the contribution of metals detected in the washwater intake. Comparison of the metals measured in washwater discharged by the *Zaandam* during scrubber trials to the EPA acute and chronic NRWQCs suggests that scrubbers may emit washwater with arsenic, copper, lead, nickel and selenium concentrations that could pose a risk to the environment. During scrubber trials aboard the *Pride of Kent*, copper, lead, nickel and zinc<sup>11</sup> were measured in washwater discharge at concentrations exceeding NRWQCs. Washwater discharged by the *Suula* was reported to contain less than 60 mg/L of total metals (the sum of cadmium, copper, nickel, lead, zinc, arsenic, chromium and vanadium). This concentration greatly exceeds the NRWQCs for any of these metals (or even the approximately 1 mg/L sum of the NRWQCs for all of these metals except vanadium); therefore, exceedances of NRWQCs for the several metals parameters, in each of the scrubber trials, suggest that scrubbers may emit washwater with concentrations of metals that could pose a risk to the environment.

## 6.7 SUMMARY

A number of constituents found in EGCS washwater discharges have been evaluated to determine whether these discharges could cause an exceedance of any NRWQC. The protectiveness of the IMO Guideline washwater limits were also evaluated in terms of whether they adequately mitigate the potential for washwater discharges to result in ecological or human health risk.

Based on this evaluation, several metals (including arsenic, copper, lead, nickel and selenium) and PAHs (chrysene, benz(a)anthracene and benzo(a)pyrene) were measured in washwater discharges at end-of-pipe concentrations that exceeded the NRWQC for that chemical. Accordingly, these parameters have the potential to contribute to an exceedance of water quality standards on a localized scale. The IMO Guideline washwater limits intended to address turbidity and PAH-phenanthrene equivalents may not be sufficiently protective, based upon the available monitoring data (EGCSA, 2010).

The pH of EGCS washwater discharges may also be a concern, because wet scrubbing involves the transfer of SO<sub>x</sub> from exhaust gasses to washwater, which is accompanied by a

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<sup>11</sup> Zinc concentrations were suspected to be an artifact introduced by sample contamination.

significant increase in acidity. The increased acidity must be neutralized, either by the natural alkalinity in seawater or by adding an alkaline chemical to freshwater. The monitoring data from scrubber trials onboard ships demonstrate that washwater neutralization is generally effective, although large volumes of reaction water may be required in open systems depending on the alkalinity of the water body. The IMO Guideline washwater limits for pH may be protective, both at sea and in confined harbors (EGCSA, 2010).

The IMO Guidelines require continuous measurement of washwater turbidity to monitor the operation of the scrubber and the washwater treatment system. For example, washwater turbidity declined from inlet to discharge onboard one vessel conducting scrubber trials; however, it is not clear that monitoring turbidity serves as a surrogate for other washwater constituents of concern (HA & H-K, 2010).

Total hydrocarbon concentrations in washwater discharges were low or below detection in the scrubber trials, despite the observation of a visible sheen accompanied by sooty deposits in the washwater discharge plume in one of these trials. Two other washwater parameters, nitrate and sulfate, appear unlikely to cause a concern because the quantities of these parameters that have been measured in EGCS washwater discharges should be readily assimilated in marine and estuarine receiving waters. In the case of nitrate, most of the EGCS washwater loading (1 to 3 kg/d/vessel, based on monitoring during trials) would be deposited to the receiving water via the atmosphere if scrubbers were not used<sup>12</sup>.

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<sup>12</sup> The nitrate in scrubber washwater is derived from the oxidation of atmospheric nitrogen as well as nitrogen in fuel that occurs during combustion. As such, NO<sub>x</sub> and nitrate emissions are unaffected by the sulfur content of the fuel and switching to low-sulfur fuels will not reduce these emissions. Consequently, compliance with MARPOL Annex VI via the two SO<sub>x</sub> control strategies (fuel switching and EGCS) result in roughly comparable loadings of nitrate to receiving waters (see calculation and discussion of Baltic Sea nitrate loading in Section 6.4).

## SECTION 7

## ACRONYMS

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### Organizations and Associated Initiatives

AEA	AEA Energy & Environment Consulting Group
DNV	Det Norske Veritas
EGCSA	Exhaust Gas Cleaning Systems Association
EPA	Environmental Protection Agency
MEPC	Marine Environment Protection Committee
MARPOL	International Convention for the Prevention of Pollution From Ships
SECA	Sulfur Oxide Emission Control Area
EU	European Union
IMO	International Maritime Organization
NRWQC	National recommended water quality criteria
GESAMP	Group of Experts on the Scientific Aspects of Marine Environmental Protection
VGP	Vessel General Permit
ETM	EGCS Technical Manual
CORMIX	Cornell Mixing Zone Expert System
OSPAR	Administrator of the Oslo and Paris Conventions for the protection of the marine environment of the northeast Atlantic

### Chemical abbreviations

SO <sub>x</sub>	Sulfur oxides (SO <sub>2</sub> and SO <sub>3</sub> )
NO <sub>x</sub>	Nitrogen oxides (NO and NO <sub>2</sub> )
PAH	Polycyclic aromatic hydrocarbon
BETX	Benzene, toluene, ethylbenzene and xylene
PAHphe	Polycyclic aromatic hydrocarbon phenanthrene equivalence concentration
TPH-D/G	Total petroleum hydrocarbon –diesel and gasoline components
DIN	Dissolved inorganic nitrogen
THC	Total hydrocarbon
TKN	Total Kjeldahl nitrogen
HEM	Hexane extractable material
COD	Chemical oxygen demand
TSS	Total suspended solids

### Units of measure

MGD	Million gallons per day
MW	Megawatt

MWh	Megawatt-hour
PPB	Parts per billion
t	Metric ton
FNUkt	Formazin nephelometric units Kilotons
NTUFNU	Nephelometric turbidity units Formazin nephelometric units
NTU	Nephelometric turbidity units
EGCS	Exhaust gas cleaning system
PMEGCS	Particulate matter Exhaust gas cleaning system
PECPM	Predicted environmental concentration Particulate matter
PNECPEC	Predicted no effect concentration Predicted environmental concentration
EACPNEC	Ecotoxicological assessment criteria Predicted no effect concentration
GC-MSEAC	Gas chromatography-mass spectrometry Ecotoxicological assessment criteria
AWPGC-MS	Advanced wastewater purification Gas chromatography-mass spectrometry
MSAWP	Motor ship Advanced wastewater purification
MS	Motor ship

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## SECTION 8

## REFERENCES

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